

A Time Base Generator with Digital Readout of Nuclear Magnetic Resonance Line Positions

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THE USE OF an X-Y recorder as a readout device with Varian HR-60 high resolution nuclear magnetic resonance (NMR) spectrometers is well established. In this application the X-axis is driven by an external time base. Spectral calibration is normally accomplished by the sideband technique (1, 2). Line positions are measured by first obtaining a scale factor between the frequency scale and linear distance. The linear distance is measured from each NMR line to the reference line. The value of the linear distance multiplied by the scale factor yields the line position in terms of frequency (cycles per second).

Several disadvantages are inherent in this method of measuring NMR line positions, not the least of which is the amount of time involved. The chief characteristic which affects the accuracy of the NMR line positions is the linearity of the external time base and/or of the recorder. Commercial recorders generally possess linearity of the order of 0.1 to 0.2% of full scale. If the linearity of the external time base is greater than the recorder linearity (considering only the readout device), the accuracy of the line positions is limited only by the linearity of the recorder. The inherent nonlinearity of the slidewire accounts at least in part for the nonlinearity of the recorder. The device described herein provides a more accurate and convenient method for measuring NMR line positions

through the use of an operational amplifier in two modes of operation.

The accuracy of NMR line position measurements can be increased in two ways: improving time base linearity and avoiding slidewire nonlinearity. Consider first time base linearity which may be defined as constancy in the time rate of change of a ramp voltage. An excellent method for the production of a linear ramp voltage is the integration of a constant voltage. Assuming in principle that this method will yield a precisely linear ramp voltage, one can see that in practice the linearity of the time base depends upon the specifications of the electronic devices used. We have designed a time base generator of improved linearity using a solid state voltage source with a low temperature coefficient and a high gain, chopper-stabilized operational amplifier.

Consider now the inherent nonlinearity of recorder slidewires. Nonlinearity is the result of the fact that the resistance of the wire per unit distance is not constant. Therefore, when one attempts to correlate voltage with linear distance, using another scale which possesses a linearity different from that of the slidewire, the result is a certain unavoidable error. This error can be avoided by driving the pen through the same distance along the same portion of slidewire by means of an accurate voltage source and then correlating that voltage with distance. The necessity of measuring distance on

the chart paper is thereby eliminated, since for a given recorder range the voltage necessary to reach a given point on the slidewire is now known. This voltage can be correlated with the quantity plotted along the abscissa. However, to achieve the greatest possible accuracy in measuring line positions the measurement should be made before the chart has been removed from the recorder. By employing this principle we have devised a method which provides a fast digital readout of NMR line positions in terms of frequency.

EXPERIMENTAL

The device consists of a combination of two modes of operation of an operational amplifier (Dymec Model DY-2460A-M1 with Model DY-2461A-M5 blank plug-in; 2-p.p.m. d.c. gain accuracy including linearity)—i.e., integration of a constant voltage and +1 gain amplification. A schematic representation is given in Figure 1. A photographic view of the time base generator constructed in this laboratory is given in Figure 2. For the integration mode the time constant is 100 seconds. Since stability of the time constant is important, a 10-megohm metal film resistor and a 10- μ f. polystyrene capacitor were used. Proper connections for the Dymec 2460A operational amplifier can be found in the Dymec instruction manual.

Ramp voltage linearity depends upon the voltage source stability. To pro-

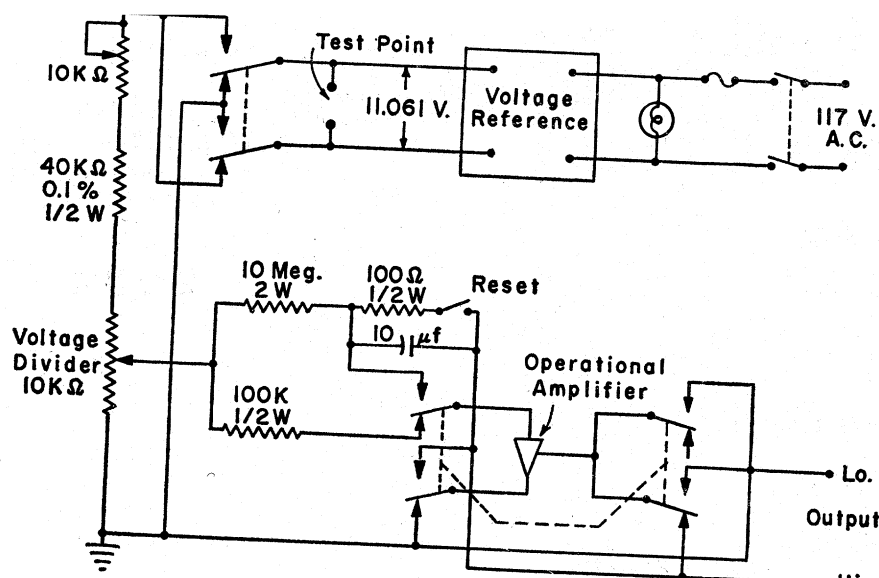


Figure 1. Circuit diagram for time base generator with digital readout of NMR line positions

vide the greatest stability a solid state voltage reference source (CircuitDyne Corp. Model PRIB-115-11.0 G) with a temperature coefficient of $\pm 0.001\%$ was chosen. The 11.061-volt output of the voltage source is reduced by means of a 40K ohm resistor and a 10K Trimpot in series with a 10K ohm, four-decade voltage divider (General Resistance Co. Dial-A-Vider Model DV-4004; linearity at one watt is ± 40 p.p.m.). Adjustment of the voltage across the decade divider to 2.0000 volts is accomplished by the Trimpot. The output of the voltage divider is variable in decade fashion from 0.0000 to ± 2.0000 volts. With the selection of this voltage a variation of pen speeds from a maximum of 5 seconds per inch to a minimum of 2.7 days per inch can be achieved. Immediately following the voltage source a DPDT (ON-OFF-ON) switch is employed as a polarity reversing switch so that the recorder pen may be driven in either direction or may be stopped in any position. The right to left direction, which is not included on commercial recorders, is more convenient for the recording of NMR spectra. Convenience results because the recording of the spectrum can commence at the reference line (usually tetramethylsilane) at the right-hand side of the chart. The spectrum is displayed according to the usual convention, except that the ringing will

be on the low field side of the various lines.

The conversion from one mode of operation to the other is accomplished by means of a four-pole, double-throw (ON-ON) switch. One advantage of this type of time base over one produced by a motor driven potentiometer is that the former permits rapid return of the pen to zero position. This is accomplished by a normally-open push button switch which short circuits the capacitor. A banana jack is connected across the output of the voltage reference supply and is mounted on the front panel as a convenient reference voltage source for other purposes, such as calibrating other instruments.

DISCUSSION

For the time base mode (with the four pole, double throw (ON-ON) switch in the proper position) the pen speed is determined by the settings of the voltage divider and the recorder X-axis range. The direction of pen travel is determined by the position of the DPDT (ON-OFF-ON) switch. Control of whether the pen touches the paper is retained in the recorder so that, if desired, the pen may be driven along the X-axis without touching the paper.

NMR line position measurements are made in the following manner: The chart paper with the spectrum is placed on the recorder platen, using the vacuum hold-down. With the pen up, the decade divider set at 0.0000 and the DPDT (ON-OFF-ON) switch in either ON position the point of the pen is visually aligned with the center of the reference peak. Then the side band frequency is dialed on the decade divider—e.g., 624.8 c.p.s., the decimal point occurring between the third and fourth decades. The pen is then visually aligned with the center of the side-band peak by adjusting the recorder X-axis range control and vernier. Finally, the decade divider is dialed until each NMR line in turn is visually aligned with the pen point. The reading on the divider is the line position in terms of frequency (c.p.s.).

The time base output has a linearity of 0.02% of full scale or better. As the voltage accumulated at a given voltage divider setting time measurements were made at increments of 1 volt. Two time-voltage pairs were used to determine the equation of a straight line. Voltages corresponding to the remaining time measurements were calculated and compared with the observed values. The reproducibility is 0.03% of full scale or better. For a given setting of the voltage divider, the accumulated output ramp voltage both negative and positive at 1000 seconds was measured to the nearest 0.1 mv. The reproducibility figure was calculated by dividing twice the standard deviation of the voltage measurements by the mean value of the output ramp voltage.

The line position (+1 gain) output has a linearity of 0.0075% or better. The voltage corresponding to each digit of the first decade of the voltage divider was measured. Two divider setting-voltage pairs were used to determine a straight line. Voltages corresponding to the remaining divider settings were calculated and compared with the observed values.

A comparison of the conventional and the electronic (described above) methods of measuring NMR line positions is shown in Table I, which gives two average values of the line position in terms of c.p.s. from tetramethylsilane

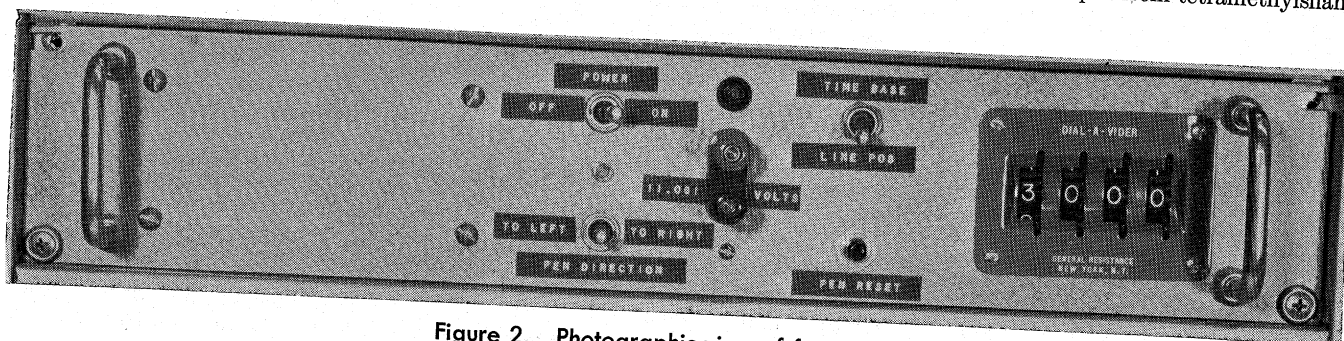


Figure 2. Photographic view of front panel

and the corresponding standard deviations for each line. Ten recordings of each spectrum were obtained at room temperature, using a Varian DP-60 spectrometer. To avoid signal saturation the radio field amplitude was set 60 db, below one-half watt. The external magnetic field was swept at the rate of 0.5 to 1.0 c.p.s./second. Spinning 5-mm. o.d. sample tubes were used to achieve maximum field homogeneity. Calibration of the spectra was accomplished by the usual side-band technique, using a Hewlett-Packard 200 CD wide band oscillator and a 522B counter. Tetramethylsilane (K & K Laboratories Inc., Jamaica, N. Y.) was used as an internal reference.

Several advantages attend the use of the time base generator described above. In addition to improved linearity and reproducibility, the time base generator affords greater convenience in the recording of NMR spectra, since the pen may be driven in the right-to-left direction. By convention NMR spectra are displayed with magnetic field strength increasing from left to right. Using tetramethylsilane as an internal reference, the reference signal normally occurs further upfield than all other spectral lines. Therefore, one can begin

Table I. Comparison of Two Methods of Measuring NMR Line Positions

	Conventional method		Electronic method	
	Line ^a position	Std. dev. ^b	Line ^a position	Std. dev. ^b
1,1,2-Trichloroethylene	387.4	0.32	387.3	0.21
Chloroform	434.5	1.44	434.8	0.30
Methylene of ester group of ethylcyanoacetate	243.3	1.25	243.4	0.50
	250.3	1.20	250.6	0.64
	257.7	1.17	257.8	0.60
	264.8	1.14	264.9	0.57
	197.8	0.73	197.8	0.70
Methanol	202.8	0.76	202.9	0.75
	252.9	0.78	252.7	0.77
	258.0	0.89	258.0	0.70
	263.0	0.89	263.2	0.75
	268.3	0.88	268.2	0.75
	216.8	1.32	216.2	0.70

Methoxy group of methyl butyrate

^a c.p.s. from tetramethylsilane, solvent-CCl₄

^b Two sigma values.

at the beginning with only an irrelevant change in the appearance of the spectrum.

The possibility of error due to the nonlinearity of the recorder slidewire has been eliminated. Consequently, line position measurements are more precise. Convenience also is achieved by correlating voltage with linear distance along the recorder slidewire. Linear distance on the chart paper need

not be measured. Also, line positions are rapidly measured in digital form in terms of frequency.

LITERATURE CITED

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- (2) Arnold, J. T., Packard, M. E., *J. Chem. Phys.* 19, 1608 (1951).

Mention of commercial products does not constitute an endorsement by the U. S. Department of Agriculture over others of a similar nature not mentioned.